

# PATENT ABSTRACTS OF JAPAN

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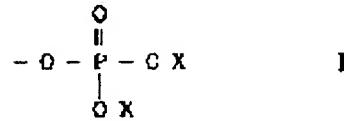
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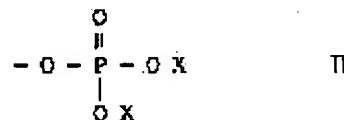
## (54) PRODUCTION OF PAPER OF PAPERBOARD

### (57)Abstract:

PROBLEM TO BE SOLVED: To obtain a paper or a paperboard, good in fixing property to a pulp and excellent in paper force strength by making the paper after adding a (meth)acrylamide-based water dispersible high molecular weight material containing a specific phosphoric acid group to the pulp slurry containing a prescribed amount of calcium ion.



SOLUTION: This method for producing a paper or a paperboard comprises making the paper after adding preferably 0.1-1wt.% (based on the solid portion of a pulp) (meth)acrylamide-based water dispersible high molecular weight material containing a phosphoric acid group of formula I (X is H, a 1-4C hydrocarbon or an alkali metal) as a paper force strength reinforcing agent to the pulp slurry containing 50-5000ppm calcium ion. Further, the (meth)acrylamide- based water dispersible high molecular weight material containing the phosphoric acid group is preferably a water dispersible high molecular weight material consisting of (meth)acrylamide and a monomer containing phosphoric acid group of formula II (X is H, a 1-6C hydrocarbon or an alkali metal) as main constituting components. Also, pH of the paper making system can be applicable from an acid region to an alkaline region.



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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to the manufacture approach of paper or the paper board. In detail, calcium ion is related with the approach of manufacturing the paper or the paper board which has the outstanding paper durability reinforcement, also in the paper-making system which exists so much.

#### [0002]

[Description of the Prior Art] In recent years, as for the supply situation of the bolt which is the raw material of paper, it has been [ steadily worsening ] a technical problem with the important increment in the rate of an use rate of used paper. Moreover, closed \*\* in the manufacture process of paper or the paper board is the situation which is not avoided by part of an environmental cure, and paper-making conditions, such as deterioration of water quality and a rise of water temperature, are getting worse increasingly in connection with it. The calcium-carbonate concentration in a paper-making system increases, and calcium ion exists in the paper-making system so much as the amounts of use, such as magazine used paper, increase especially or carbonation of a paper-making system progresses.

[0003] Moreover, in the paper manufacture process of such paper or the paper board, the acrylamide system polymer of anionic, cationicity, or both sexes is conventionally used widely as a paper reinforcing agent. Fixable [ to the pulp of a paper reinforcing agent ] falls, and it is becoming impossible however, to discover the effectiveness as a paper reinforcing agent enough by closed \*\* of the increment in the rate of a used paper compounding ratio, or wastewater, as a result of a lot of impurity's (calcium ion's etc.) existing in a paper-making system. That is, although the acrylamide system polymer paper reinforcing agent with ionicity is fixed to pulp with electrostatic attraction, if calcium ion exists so much, the desired paper durability enhancing effect is not acquired.

#### [0004]

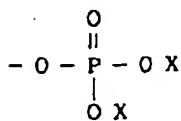
[Problem(s) to be Solved by the Invention] As for this invention, also in the paper-making system in which calcium ion exists so much, fixable [ to pulp ] is good, and it aims at offering the approach of manufacturing the paper or the paper board which has the outstanding paper durability reinforcement.

#### [0005]

[Means for Solving the Problem] As a result of repeating examination wholeheartedly, when using the acrylamide (meta) system water-dispersion macromolecule which contains a specific phosphoric-acid radical as a paper reinforcing agent that the technical problem of said conventional technique should be solved, this invention persons came to complete a header and this invention for the ability of the paper or the paper board which has the outstanding paper durability reinforcement to be manufactured, even if calcium ion was the paper-making system which exists so much.

[0006] That is, this invention is general formula (1): [0007] as a paper reinforcing agent to the pulp slurry containing 50 ppm - 5000 ppm of calcium ion.

[Formula 5]



[0008] (-- the inside of a formula and X are the same respectively -- or it differs and the hydrocarbon group or alkali-metal atom of a hydrogen atom and carbon numbers 1-4 is expressed.) -- after adding the acrylamide (meta) system water-dispersion macromolecule containing the phosphoric-acid radical expressed, it is related with the manufacture approach of the paper or the paper board characterized by carrying out paper making.

[0009]

[Embodiment of the Invention] The acrylamide (meta) system water-dispersion macromolecule containing the phosphoric-acid radical expressed with said general formula (1) of this invention is a water-dispersion macromolecule obtained by carrying out the polymerization of the acrylamide (meta), and if said phosphoric-acid radical is contained in the water-dispersion macromolecule concerned, especially the approach of introducing said phosphoric-acid radical will not be limited.

[0010] The acrylamide (meta) system water-dispersion macromolecule containing such a phosphoric-acid radical copolymerizes the monomer containing the phosphoric-acid radical expressed with acrylamide (meta) and said general formula (1) as a main constituent, and is obtained.

[0011] Although it sets to this invention, and it can be independent-used or these good (it is the same semantics as (meta) hereafter) can use acrylamide or methacrylamide together with acrylamide (meta), it is good to carry out independent use of the acrylamide from the field of economical efficiency.

[0012] moreover, as an example of the monomer containing the phosphoric-acid radical expressed with said general formula (1) For example, polyethylene-glycol (meta) acrylate phosphate, 2-(diethoxy phosphinyl) (oxy-) ethyl (meta) acrylate, Bis(meta) (bitter taste roil oxy-ethyl) hydro gene phosphate, Monochrome (2-(meta) acryloyloxyethyl) acid phosphate, Diphenyl-2-(meta) AKURO yloxy ethyl phosphate, 2-hydroxyethyl (meta) bitter taste roil phosphonic acid, 2-(meta) acrylamide-isobutane phosphonic acid, these alkali-metal salts, etc. are raised.

[0013] each amount of the monomer used in the case of copolymerizing the phosphoric-acid radical content monomer expressed with the aforementioned (meta) acrylamide and said general formula (1) as a main constituent -- the total mol sum of a monomer -- receiving -- usually -- acrylamide (meta) -- about 90-99.9 mol % -- desirable -- about 92-99.5 mol % -- it is -- on the other hand -- a phosphoric-acid radical content monomer -- about 0.1-10 mol % -- it is 0.5 - eight-mol % preferably.

[0014] moreover, the monomer in which the acrylamide (meta) system water-dispersion macromolecule containing the phosphoric-acid radical of this invention contains the phosphoric-acid radical expressed with the aforementioned (meta) acrylamide and said general formula (1) -- in addition, what copolymerizes the anionic monomer except the monomer containing the phosphoric-acid radical expressed with a cationic monomer and/or said general formula (1) as a main constituent, and is obtained is included. The acrylamide (meta) system water-dispersion macromolecule which copolymerized these ionicity monomer is desirable at the point fixable [ whose / to pulp ] improves.

[0015] The vinyl monomer which contains the quaternary ammonium salt obtained by the reaction of the salts of inorganic acids, such as dimethylaminoethyl (meta) acrylate, diethylaminoethyl (meta) acrylate, dimethylaminopropyl (meta) acrylamide, and diethylamino propyl (meta) acrylamide, or an organic acid or this the 3rd class amino-group content vinyl monomer, and the fourth class-sized agents, such as methyl chloride, benzyl chloride, a dimethyl sulfate, and epichlorohydrin, as a cationic monomer, for example is raised.

[0016] Moreover, as an anionic monomer except the monomer containing the phosphoric-acid radical expressed with said general formula (1), the sodium salt of organic sulfonic-acids [, such as dicarboxylic acid; vinyl sulfonic acids, such as monocarboxylic acid; maleic acids, such as an acrylic acid (meta) and a crotalic acid a fumaric acid, an itaconic acid, muconic acid, and a citraconic acid a styrene sulfonic acid, a metallyl sulfonic acid, and 2-acrylamido-2-methyl propane sulfonic acid, ]; or these various organic acids, potassium salt, etc. are raised, for example.

[0017] The amount of each monomer used in the case of using the anionic monomer except the monomer containing the phosphoric-acid radical expressed with a cationic monomer and/or said general formula (1) is as follows to the total mol sum of a monomer. namely, -- usually -- acrylamide (meta) -- about 80-99.8 mol % -- it is about 80-99.4 mol % preferably. When not filling to 80-mol%, it is hard to have sufficient paper durability effectiveness. on the other hand -- a phosphoric-acid radical content monomer -- about 0.1-10 mol % -- it is 0.5-8-mol % preferably. moreover, total of the monomer which contains preferably the phosphoric-acid radical expressed with an anionic monomer and a general formula (1) concerned when using the anionic monomer except the monomer which contains about 0.1-10 mol % and the 0.2-8-mol phosphoric-acid radical which is % and is expressed with said general formula (1) when a cationic monomer is used for the amount of the ionicity monomer used -- 0.1 - ten-mol % -- it is 0.2 - eight-mol % preferably.

[0018] Furthermore, in addition to said monomer, the acrylamide (meta) system water-dispersion macromolecule of this invention can copolymerize a cross-linking monomer and other monomers as a constituent as occasion demands in the range which does not have a bad influence on the engine performance.

[0019] As a cross-linking monomer, the vinyl polymer which has chain transfer nature substituents, such as 4 functionality monomers, such as 3 organic-functions monomers, such as 2 organic-functions monomer [, such as ethylene glycol di(metha)acrylate, a diaryl amine, and N-methylol acrylamide ], triaryl isocyanate, N, and N-diaryl acrylamide, and tetra-allyloxy ethane, and allyl compound (meta) acrylate, diethylene-glycol monochrome (meta) acrylate, dimethyl acrylamide, is raised, for example. the case where a cross-linking monomer is used -- the amount used -- the total mol sum of a monomer -- receiving -- usually -- or less about 5 mol % -- it is less than [ 2 mol % ] preferably. The copolymer obtained becomes gel and is not desirable when exceeding five-mol %.

[0020] As other monomers, the ester of anionic monomers, such as N permutation (meta) acrylamides, such as t-octyl acrylamide, an acrylic acid (meta), and a maleic acid, and alcohol, styrene, alpha methyl styrene, vinyltoluene, acrylonitrile, the methyl vinyl ether, isopropyl acrylamide, vinyl acetate, an alpha olefin, etc. are raised, for example. the case where other monomers are used -- the amount used -- the total mol sum of a monomer -- receiving -- or less about 10 mol % -- it is less than [ 8 mol % ] preferably. In exceeding ten-mol % (meta), the rate of acrylamide decreases, and the paper which has sufficient paper durability effectiveness is hard to be obtained.

[0021] Various well-known approaches can be conventionally used for the method of copolymerizing said monomer and obtaining the acrylamide (meta) system water-dispersion macromolecule of this invention. For example, said each monomer and water can be taught to a predetermined reaction container, the usual radical polymerization initiators, such as a redox system polymerization initiator of the form which combined persulfate, such as potassium persulfate and ammonium persulfate, or these and the reducing agent like a sodium hydrogensulfite, can be added, and the acrylamide (meta) system water-dispersion macromolecule of this invention can be obtained by warming under churning.

[0022] The weight average molecular weight of the obtained acrylamide (meta) system water-dispersion macromolecule is usually 100,000 to about 10 million, and viscosity is converted into 10 % of the weight of solid content concentration, and is usually the description below 20000cps (25 degrees C) extent preferably below 30000cps (25 degrees C) extent.

[0023] The manufacture approach of the paper of this invention or the paper board calcium ion to the pulp slurry included 50 ppm - 5000 ppm It is what is characterized by carrying out paper making after adding the aforementioned (meta) acrylamide system water-dispersion macromolecule as a paper reinforcing agent. The pulp slurry contains a lot of calcium ion, and the same conditions as the manufacture approach of the common paper or the common paper board can be adopted except using the acrylamide (meta) system water-dispersion macromolecule of said specific ionicity as a paper reinforcing agent.

[0024] Namely, what is necessary is just to usually add a paper reinforcing agent to pulp solid content at about (solid content) 0.1 - 1% of the weight of an operating rate. Moreover, the addition stage of a paper reinforcing agent can be set up suitably, and ranging from the acidic range to alkalinity, pH of a paper-

making system reaches far and wide, and can be applied. Moreover, if it determines suitably according to paper-making conditions, it is sufficient for the class of pulp, and the class of paper-making Hakusui, and they can carry out combination addition of a sizing compound, a fixing agent, the loading material, etc. suitably.

[0025] In addition, the calcium ion concentration in a pulp slurry is the value measured with the pocket water quality meter made from LASA (Cuvette Test LCK327).

[0026]

[Effect of the Invention] the paper-making system in which calcium ion exists so much according to this invention -- also setting -- a ratio -- the paper or the paper board which has paper durability reinforcement, such as bursting strength, breaking length, and surface reinforcement, can be offered.

[0027]

[Example] Hereafter, an example and the example of a comparison are given and this invention is explained more concretely. In addition, each of sections and %s is based on weight criteria.

[0028] The ion-exchange-water 500 section was taught to the flask equipped with example of manufacture 1 agitator, a dropping funnel (A), a dropping funnel (B), a thermometer, a reflux cooling pipe, and nitrogen gas installation tubing. On the other hand, the ammonium persulfate 0.21 section and the ion-exchange-water 100 section were taught to the dropping funnel (A) for the acrylamide 170 section, the ion-exchange-water 230 section, and the monochrome (2-methacryloiloxy-ethyl) acid phosphate 14 section as a polymerization initiator at the dropping funnel (B). After removing the oxygen in all the systems of reaction through nitrogen gas, the inside of the system of reaction was heated to 80 degrees C under churning, and it was dropped at it from the dropping funnel (A) and the dropping funnel (B) from the time of becoming 80 degrees C, having applied it to coincidence for 2 hours. Subsequently, ion exchange water was added and the water dispersion of 10.4% of solid content and an acrylamide system macromolecule with a viscosity of 7300cps was obtained.

[0029] In the example 1 of example of manufacture 2 manufacture, except having changed into the acrylamide 159 section, the ion-exchange-water 230 section, the dimethylaminopropyl acrylamide 15.6 section, the 80% acrylic-acid 4.5 section, and the monochrome (2-methacryloiloxy-ethyl) acid phosphate 14 section what was taught to the dropping funnel (A), the same actuation as the example 1 of manufacture was performed, and the water dispersion of 10.4% of solid content and an acrylamide system macromolecule with a viscosity of 8500cps was obtained.

[0030] In the example 3 of manufacture - the example 1 of 8 manufactures, as shown in Table 1, even if few [ either ] among the class of monomer component, or its amount used (presentation ratio: mol %), a kind was changed, and also the same actuation as the example 1 of manufacture was performed, and the water dispersion of an acrylamide system macromolecule was obtained. the description of each obtained water dispersion -- a value is shown table 2.

[0031]

[Table 1]

	組成(モル%)				
	AM	アニオン性モノマー	カチオン性モノマー	リン酸基含有モノマー	その他のモノマー等
製造例1	96.0	_____	_____	PM 4	_____
製造例2	92.0	AA 2	DMAPAA 4	PM 2	_____
製造例3	92.0	_____	DMAPAA 4	PM 4	_____
製造例4	91.5	_____	DMAPAA 4	PM 4	DMAA 0.5
製造例5	92.0	_____	DM 4	PM 4	_____
製造例6	96.0	AA 4	_____	_____	_____
製造例7	92.0	AA 4	DMAPAA 4	_____	_____
製造例8	92.0	AA 4	DM 4	_____	_____

[0032] The inside of Table 1, AM:acrylamide and PM:monochrome (2-methacryloiloxy-ethyl) acid phosphate, AA:acrylic acid, DMAPAA:dimethylaminopropyl acrylamide, DM:dimethylaminoethyl methacrylate, DMAA: Dimethyl acrylamide is shown.

[0033]

[Table 2]

	性状	
	固形分(%)	粘度(cps)
製造例1	10.4	7300
製造例2	10.3	8500
製造例3	10.5	8800
製造例4	10.8	5500
製造例5	10.8	7900
製造例6	10.4	6500
製造例7	10.4	7300
製造例8	10.5	6100

[0034] the example BKP of reference -- a Niagara style -- after adding a sodium carbonate as a pH regulator to the pulp which carried out beating with the beater and which was adjusted to Canadian standard freeness (C. S.F) 550ml -- further -- a sulfuric-acid band -- 0.5% for pulp -- the water dispersion of each acrylamide system macromolecule obtained in each example of manufacture which is added and is shown subsequently to Table 3 -- a paper reinforcing agent -- carrying out -- 0.5% for pulp -- it added, and it agitated and mixed to homogeneity. The obtained pulp slurry (pH6.5) is diluted to 0.5%, and it is basis-weight 100 g/m<sup>2</sup> with the TAPPI sheet machine. Paper making is carried out so that it may become, and it is 5 kg/m<sup>2</sup>. Press dehydration was carried out for 2 minutes. Subsequently, in 100

degrees C, it dried for 4 minutes with the rotation mold dryer, and gas conditioning was carried out in 20 degrees C and 65%R.H. for 24 hours.

[0035] Beating is carried out with a beater. examples 1-2 and the example 1 of a comparison - 2B KP -- a Niagara style -- To the pulp adjusted to Canadian standard freeness (C. S.F) 550ml So that the amount of calcium ion may serve as predetermined concentration shown in Table 4 or 5 to a pulp slurry, after adding a sodium carbonate as a pH regulator a calcium chloride -- adding -- further -- a sulfuric-acid band -- 0.5% for pulp -- the water dispersion of each acrylamide system macromolecule obtained in each above-mentioned example of manufacture which is added and is shown subsequently to Table 4 or 5 -- a paper reinforcing agent -- carrying out -- 0.5% for pulp -- it added, and it agitated and mixed to homogeneity. The obtained pulp slurry (pH6.5) is diluted to 0.5%, and it is basis-weight 100 g/m<sup>2</sup> with the TAPPI sheet machine. Paper making is carried out so that it may become, and it is 5 kg/m<sup>2</sup>. Press dehydration was carried out for 2 minutes. Subsequently, in 100 degrees C, it dried for 4 minutes with the rotation mold dryer, and gas conditioning was carried out in 20 degrees C and 65%R.H. for 24 hours.

[0036] The rate of fixing (%) and T mold peel strength (g/cm) were measured about the paper obtained in the example of reference, examples 1-2, and the examples 1-2 of a comparison. A result is shown in Tables 3-5.

[0037] (Rate of fixing) The nitrogen content of the obtained paper was measured and the rate of fixing to pulp was computed. Rate (%) of fixing = (B-C) / Ax100. A: Nitrogen measured value of the applied acrylamide system water-dispersion macromolecule, B : nitrogen measured value of the paper which added and carried out paper making of the acrylamide system water-dispersion macromolecule, nitrogen volume measured value of the paper which added and carried out paper making of the acrylamide system water-dispersion macromolecule using the same pulp as C:B.

[0038] (T character peel strength) J.Tappi It measured according to No.19-m.

[0039]

[Table 3]

	カルシウム化合物		なし	
	カルシウムイオン濃度(ppm)		0. 1	
	水分散性高分子		定着率 (%)	T字剥離強度 (g/cm)
	種類	イオン性		
参考例	製造例 1	アニオニ性	69. 0	28. 5
	製造例 2	両性	83. 5	32. 9
	製造例 3	両性	84. 1	33. 3
	製造例 4	両性	84. 3	33. 8
	製造例 5	両性	82. 0	32. 5
参考例	製造例 6	アニオニ性	66. 7	27. 7
	製造例 7	両性	83. 7	31. 4
	製造例 8	両性	81. 5	30. 4

[0040]

[Table 4]

	カルシウム化合物		塩化カルシウム	
	カルシウムイオン濃度(ppm)		50	
	分散性高分子		定着率 (%)	T字剥離強度 (g/cm)
	種類	イオン性		
実施例1	製造例1	アニオン性	68.0	29.5
	製造例2	両性	80.5	31.8
	製造例3	両性	81.6	32.5
	製造例4	両性	81.3	31.6
	製造例5	両性	79.3	31.2
比較例1	製造例6	アニオン性	51.7	26.2
	製造例7	両性	76.7	30.4
	製造例8	両性	75.5	29.6

[0041]  
[Table 5]

	カルシウム化合物		塩化カルシウム	
	カルシウムイオン濃度(ppm)		1000	
	分散性高分子		定着率 (%)	T字剥離強度 (g/cm)
	種類	イオン性		
実施例2	製造例1	アニオン性	67.5	29.6
	製造例2	両性	77.5	30.9
	製造例3	両性	79.6	31.3
	製造例4	両性	79.3	31.0
	製造例5	両性	76.2	30.1
比較例2	製造例6	アニオン性	47.7	25.7
	製造例7	両性	65.7	28.5
	製造例8	両性	56.5	27.6

[0042] an example 3 and example of comparison 3 example 1 -- setting -- as pH regulator -- a sodium carbonate -- not adding -- instead of [ of a calcium chloride ] -- a calcium carbonate -- 20% for pulp -- paper making was carried out like the example 1 except having added (calcium ion concentration of 100 ppm in a pulp slurry).

[0043] About the paper obtained in the example 3 and the example 3 of a comparison, the rate of fixing

(%) and breaking length (km) were measured. A result is shown in Table 6.

[0044] Breaking length: JIS Tensile strength test method of the paper based on P8113, and the paper board.

[0045]

[Table 6]

	カルシウム化合物		炭酸カルシウム	
	カルシウムイオン濃度(ppm)		100	
	水分散性高分子		定着率 (%)	裂断長 (km)
	種類	イオン性		
実施例 3	製造例 8	アニオン性	71.6	3.22
	製造例 1	両性	83.3	3.42
	製造例 2	両性	83.1	3.45
	製造例 4	両性	83.5	3.45
	製造例 6	両性	81.0	3.39
比較例 3	製造例 7	アニオン性	35.7	2.89
	製造例 3	両性	70.7	3.11
	製造例 5	両性	66.5	3.05

[0046] An example 4 and example of comparison 4 corrugated-paper used paper, and magazine used paper are mixed by the weight ratio of 1:1. it -- a Niagara style, after adding a sulfuric-acid band 2% to the pulp adjusted to beating and Canadian standard freeness (C. S.F) 420ml with the beater the water dispersion of each acrylamide system macromolecule obtained in each above-mentioned example of manufacture shown in Table 7 -- a paper reinforcing agent -- carrying out -- 0.5% for pulp -- it added, and it agitated and mixed to homogeneity. The obtained pulp slurry (pH5.6, calcium ion concentration of 280 ppm) is diluted to 0.5%, and it is basis-weight 160 g/m<sup>2</sup> with the TAPPI sheet machine. Paper making is carried out so that it may become, and it is 5kg/m<sup>2</sup>. Press dehydration was carried out for 2 minutes. Subsequently, in 110 degrees C, it dried for 4 minutes with the rotation mold dryer, and gas conditioning was carried out in 20 degrees C and 65%R.H. for 24 hours.

[0047] the paper obtained in the example 4 and the example 4 of a comparison -- a ratio -- bursting strength (kPa) was measured. A result is shown in Table 7.

[0048] a ratio -- bursting strength: -- JIS Bursting strength test method by the Meulens low voltage form tester of the paper based on P8112, and the paper board.

[0049]

[Table 7]

	カルシウムイオン濃度(ppm)		280
	水分散性高分子		比破裂強度 (kPa · m <sup>2</sup> / g)
	種類	イオン性	
実施例 4	製造例 1	アニオン性	262
	製造例 2	両性	288
	製造例 3	両性	289
	製造例 4	両性	285
	製造例 5	両性	283
比較例 4	製造例 6	アニオン性	215
	製造例 7	両性	253
	製造例 8	両性	246

[0050] An example 5, and example of comparison 5BKP and coat BUROKU are mixed by the weight ratio of 7:3. it -- a Niagara style, after adding a sulfuric-acid band 1.5% to the pulp adjusted to beating and Canadian standard freeness (C. S.F) 450ml with the beater the water dispersion of each acrylamide system macromolecule obtained in each above-mentioned example of manufacture shown in Table 8 -- a paper reinforcing agent -- carrying out -- 0.5% for pulp -- it added, and it agitated and mixed to homogeneity. The obtained pulp slurry (pH6.6, calcium ion concentration of 240 ppm) is diluted to 0.5%, and it is basis-weight 100 g/m<sup>2</sup> with the TAPPI sheet machine. Paper making is carried out so that it may become, and it is 5kg/m<sup>2</sup>. Press dehydration was carried out for 2 minutes. Subsequently, in 100 degrees C, it dried for 4 minutes with the rotation mold dryer, and gas conditioning was carried out in 20 degrees C and 65%R.H. for 24 hours.

[0051] Surface reinforcement (A) was measured about the paper obtained in the example 5 and the example 5 of a comparison. A result is shown in Table 8.

[0052] Surface reinforcement: JIS It is a test method in the surface strength of the paper based on P8129, and the paper board. It is based on the approach using a wax pick.

[0053]

[Table 8]

	カルシウムイオン濃度(ppm)	240	
	水分散性高分子	表面強度	
	種類	イオン性	
実施例 5	製造例 1	アニオニン性	10
	製造例 2	両性	14
	製造例 3	両性	14
	製造例 4	両性	14
	製造例 5	両性	13
比較例 5	製造例 6	アニオニン性	7
	製造例 7	両性	11
	製造例 8	両性	10

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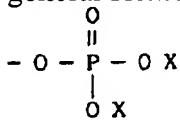
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CLAIMS

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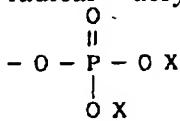
## [Claim(s)]

[Claim 1] the pulp slurry containing 50 ppm - 5000 ppm of calcium ion -- as a paper reinforcing agent -- general formula (1): -- [Formula 1]



(-- the inside of a formula and X are the same respectively -- or it differs and the hydrocarbon group or alkali-metal atom of a hydrogen atom and carbon numbers 1-4 is expressed.) -- the manufacture approach of of the paper or the paper board characterized by carrying out paper making after adding the acrylamide (meta) system water-dispersion macromolecule containing the phosphoric-acid radical expressed.

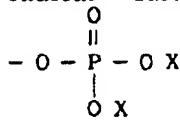
[Claim 2] the acrylamide (meta) system water-dispersion macromolecule containing a phosphoric-acid radical -- acrylamide (meta) and general formula (1): -- [Formula 2]



(-- the inside of a formula and X are the same respectively -- or it differs and a hydrogen atom, a carbon number 1 - 6 hydrocarbon group, or an alkali-metal atom is expressed.) -- the manufacture approach of of the paper according to claim 1 or the paper board which is the water-dispersion macromolecule which becomes considering the monomer containing the phosphoric-acid radical expressed as a main constituent.

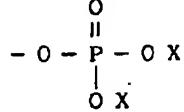
[Claim 3] The manufacture approach of of the paper according to claim 2 or the paper board which is the water-dispersion giant molecule with which the acrylamide (meta) system water-dispersion giant molecule containing a phosphoric-acid radical becomes considering a cationic monomer as a constituent further.

[Claim 4] the acrylamide (meta) system water-dispersion macromolecule containing a phosphoric-acid radical -- further -- general formula (1): -- [Formula 3]



(-- the inside of a formula and X are the same respectively -- or it differs and a hydrogen atom, a carbon number 1 - 6 hydrocarbon group, or an alkali-metal atom is expressed.) -- the manufacture approach of of the paper according to claim 2 or 3 or the paper board which is the water-dispersion macromolecule which becomes considering the anionic monomer except the monomer containing the phosphoric-acid radical expressed as a constituent.

[Claim 5] General formula (1): [Formula 4]



(-- the inside of a formula and X are the same respectively -- or it differs and a hydrogen atom, a carbon number 1 - hydrocarbon group, or an alkali-metal atom is expressed.) -- the monomer containing the phosphoric-acid radical expressed -- 0.1-10-mol% of the constituent of an acrylamide (meta) system water-dispersion macromolecule -- the manufacture approach of of the paper according to claim 2, 3, or 4 or the paper board which it comes to contain.

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[Translation done.]